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Attempts to reduce water and chemical usage in the removal of bifunctional reactive dyes from cotton: Part 2 bis(vinyl sulfone), aminochlorotriazine/vinyl sulfone and bis(aminochlorotriazine/vinyl sulfone) dyes

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ABSTRACT

Dyeings on cotton obtained using three commercial bifunctional reactive dyes were subjected to a standard, five-stage method which employed a proprietary wash-off agent as well as a three stage, chemical-free wash-off process. Dyeings obtained using both wash-off methods were of the same colour and displayed similar levels of fastness to repeated washing at 60 °C. Lowering the number of wash-off stages from five to three and replacing the wash-off agent with 98 °C water rinses reduced considerably, both the COD and, especially, BOD_5 compared with the standard wash-off method, with no increase in COD/BOD_5 ratio. The three-bath wash-off method therefore offers potential savings in water usage, compared to the standard method and also eliminates the need for chemicals to be employed in wash-off.

1. Introduction

Regardless of type of dye (eg acid, reactive, disperse, etc.) and textile fibre (eg cellulosic, wool, polyamide, etc.), an aqueous ‘wash-off’ treatment is commonly used at the end of dyeing to remove surplus dye and dyeing auxiliaries (surfactants, electrolytes, etc.), so that the desired colour, depth of shade, fastness, etc. can be secured. Typically, wash-off treatments employ specific auxiliaries (eg surfactants, alkalis, etc.) and consume large amounts of water [1].

Cotton is, by some margin, the world’s most popular natural textile fibre, as shown by the findings [2] that of the 72.6×10^6 T of fibre consumed globally in 2007, cotton comprised the largest proportion (37%) of natural fibre production (silk, wool and other natural fibres made up a very small fraction of natural fibre production) with man-made and synthetic fibres comprising 61%. Of the various classes of dye that can be used on cotton and other cellulosic fibres namely, vat, direct, reactive and azoic colorants, reactive dyes have enjoyed outstanding commercial success since their introduction in the mid 1950s, owing to their relative ease of application, wide shade gamut and brightness as well as their high wet fastness on such fibres. However, members of this dye class nevertheless possesses serious disadvantages [1], in terms of their application to cotton and other cellulosic fibres, especially from an environmental viewpoint insofar as:

- immersion (exhaustion) dyeing, which accounts for ~70% of reactive dye usage on cotton, requires the use of significant amounts of electrolyte ($\leq$100 gl^{-1});
- dye–fibre fixation is always accompanied by alkali-induced dye hydrolysis, which results in ~50–70% efficiency of fixation, depending upon dye type and depth of shade [3] as well as severe effluent problems, since ~20–50% of the applied reactive dye is discarded as coloured effluent, which also usually contains surfactants that are commonly used in the process;
- all reactive dyes containing haloheterocyclic reactive groups offer the potential of generating absorbable organic halogen (AOX) in dye effluent [4].

Reactive dyeings on cellulosic fibres require a lengthy *wash-off* treatment to remove hydrolysed dye, unfixed dye and auxiliaries. Dye makers invariably recommend specific wash-off processes for their particular dye ranges, such processes commonly involving the use of a proprietary wash-off agent; many auxiliary manufacturers offer a wide variety of wash-off agents for use with reactive dyes on

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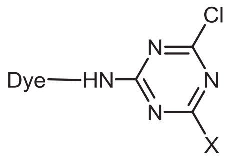
cellulosic fibres [5]. As such, the wash-off of reactive dyeings and the treatment of the resulting effluent contribute a sizeable part of the total dyeing costs (~50%) and the effluent load, mainly because of the surfactants that are commonly used in the wash-off process. A further major environmental issue surrounding the use of reactive dyes on cellulosic fibres is the high volume of water employed to remove both hydrolysed and non-reacted dye during wash-off. As outlined below, dye makers have expended vast amounts of research effort on reactive dyes and the development of commercial dye ranges for cellulosic fibres over the past 50 or so years, this having produced innumerable patents, commercial reports and research papers. However, in sharp contrast, the number of publications that relate to reactive dye wash-off are comparatively very small and, for the most part, these were not generated by dye makers, which is surprising bearing in mind the vital importance of the wash-off stage in the reactive dyeing of cellulosic fibres [6–16].

Contemporary reactive dye ranges comprise *bifunctional* dyes which are the result of systematic and, in the majority of cases, elegant, developments in both chromogen and, especially, reactive group chemistry that have spanned >50 years. Several ranges of bifunctional reactive dye are currently available, these using a variety of different reactive systems and different wash-off procedures. In this context, it was thought that a brief discussion of the development and essential features of bifunctional dyes would be useful.

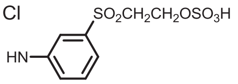
The first commercially available reactive dye ranges for cellulosic fibres, namely the dichlorotriazine *Procion M* (ICI; 1956) and the aminochlorotriazine *Procion H* (ICI) and *Cibacron* (Ciba–Geigy) ranges introduced in 1957, were *monofunctional* dyes that contained either one reactive centre, such as the chlorine group in aminochlorotriazine dyes (**1a**) or, two, equivalent reactive centres, such as the two chlorine groups in the case of dichlorotriazine dyes (**1b**). In the latter dye type, substitution of one of the displaceable halogen atoms with either *–OCell* or *–OH*, via either reaction with the substrate or hydrolysis, respectively, diminishes the reactivity of the remaining chlorine group. Other popular ranges of monofunctional reactive dye were subsequently launched [17], each employing a different reactive system, such as vinyl sulfone (*Remazol*; Hoechst), difluorochloropyrimidine (*Drimarene K*; Clariant), aminofluorotriazine (*Cibacron F*; Ciba–Geigy) as well as the vinyl sulfone *Remazol EH* (BASF) dyes for application which display easy wash-off, owing to the low substantivity of the hydrolysed form of the dye (Dye–$SO_2CH_2CH_2OH$) compared to that of the reactive variant (Dye–$SO_2CH{=}CH_2$) [18,19]. In general, the hydrolysed form of monofunctional dyes can no longer undergo dye–fibre reaction, thereby resulting in low fixation levels (~50% in heavy depths), low dye-utilisation and concomitant effluent problems, which are further exacerbated by the need for lengthy wash-off processes to remove the hydrolysed dye. Furthermore, fastness problems can also arise if monofunctional dyes, which are covalently bound to the substrate, undergo dye–fibre bond cleavage, as a result of alkaline hydrolysis (eg vinyl sulfone dyes), acid hydrolysis (eg dichlorotriazine dyes) or laundering in the presence of peroxides (eg difluorochloropyrimidine dyes).



1a X = NH-R

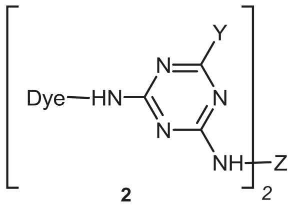
1b X = Cl

1c X =



Research efforts from the mid 1960s onwards focussed on ways of increasing dye fixation levels in exhaust dyeing, so as to address growing environmental concerns regarding the high volumes of coloured effluent produced during exhaust reactive dyeing. In this context, attention turned towards dyes that contained two reactive groups per molecule. The first ranges of *bifunctional* reactive dye were introduced in the late 1960s/early 1970s, such dyes being *homobifunctional* types in which both reactive groups were identical, as exemplified by the bis(aminochlorotriazine) *Procion H-E* (ICI) dyes (**2**; where Y is Cl and Z is a diaminoarene linking group) for exhaust dyeing. These particular were approximately twice the size of their monofunctional counterparts and therefore displayed increased substantivity (and thus enhanced exhaustion) and fixation levels, resulting in reduced levels of hydrolysis. Ranges of similar dyes are marketed by several makers, as exemplified by the:

- *Procion H-EXL* (ICI) range of bis(aminochlorotriazine) dyes, which are chemically similar to their *Procion H-E* counterparts and, of which, several employ novel linking diamines (L in **3**), and display greater reproducibility, improved levelling and superior compatibility [4];
- bis(aminonicotinotriazine) (**4**) *Kayacelon React* (Nippon Kayaku), which utilised the catalytic effect of quaternary nitrogen derivatives on the reactivity of monohalotriazines [4].
- *Cibacron LS* (Ciba–Geigy) dyes based upon bis(aminofluorotriazine) (**2**; where Y is F and Z is an alkylene linking group) although several different reactive groups in a variety of arrangements are employed, including aminochlorotriazine and monofluorotriazine in combination with vinyl sulfone [18].



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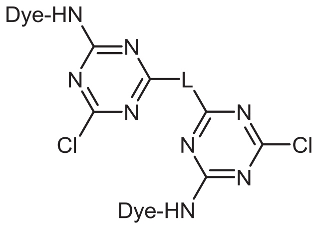

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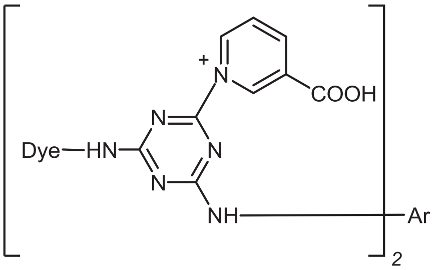

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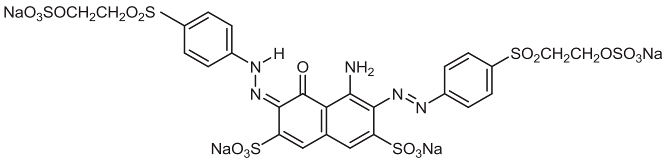
Interestingly, the earliest (and arguably the most famous) example of a homobifunctional reactive dye is the bis(β-sulfatoethylsulfone) C.I. Reactive Black 5 (**5**), which contains two masked vinyl sulfone groups per molecule. Intriguingly, whilst this dye had been introduced in the late 1950s by Hoechst as a member of its *Remazol* dye range for cellulosic fibres, the company did not at the time market a full range of *Remazol* dyes bearing two reactive groups.



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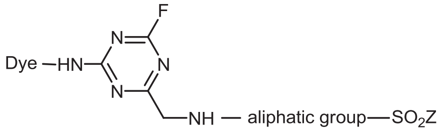
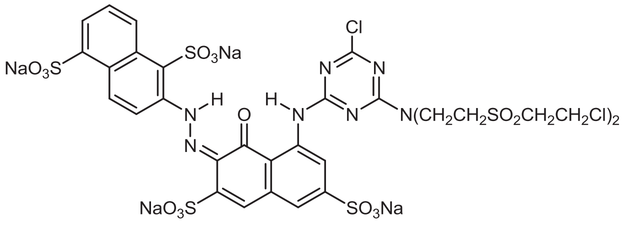
In the late 1970s/early 1980s, the first range of *heterobifunctional* reactive dyes was launched by Sumitomo, videlicet, the (aminochlorotriazine/masked vinyl sulfone) types [4,19] (**1c**; *Sumifix Supra*) which displayed high substantivity (as well as high exhaustion and fixation) imparted by the triazine group. The two dissimilar reactive groups enabled the dyes to be applied over a wide range of temperature (50 °C for the vinyl sulfone and upto 80 °C for the aminochlorotriazine), thus favouring shade reproducibility. The use of two different reactive systems resulted in higher dye-utilisation and improved fastness to acid hydrolysis and peroxide laundering [17,19]. The *Cibacron C* (Ciba–Geigy) range of mixed bifunctional dyes, introduced in the late 1980s, utilised an aliphatic vinyl sulfone group together with either a monofluorotriazine group (**6**) or an aromatic vinyl sulfone group [17,20], solubility being aided by the flexible alkanediyl ($-[CH_2]_n-$) linkage in **6**.



Z = $CH{=}CH_2$ or $CH_2CH_2OSO_3Na$

6

The use of more than two reactive groups within a dye molecule does not increase fixation efficiency owing to concomitant detrimental effects upon dye solubility, substantivity and migration [18]. Consequently, despite much patent activity, few commercial, polyfunctional reactive dyes have been marketed, two notable examples being the trifunctional C.I. Reactive Red 181 (*Remazol Red BS*; **7**) and *Cibacron Red C-2G* dyes [17,18].



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This paper concerns the reduction in the amount of water used in the wash-off of contemporary, homofunctional and heterobifunctional reactive dyes on cotton. The first part of the paper [1] showed that the five-stage, wash-off process recommended by the makers of bis(aminochlorotriazine) dyes could be replaced by a novel, chemical-free, three-bath, wash-off process that enabled both the duration of wash-off and the amounts of water and chemicals used to be reduced. This part of the paper considers bis (vinyl sulfone), aminochlorotriazine/vinyl sulfone and bis(aminochlorotriazine/vinyl sulfone) dyes on cotton. As discussed in part 1 of the paper [1], environmental indicators (BOD_5, COD and COD/BOD_5) were used to describe potential improvements in the biodegradability of the wastewater generated using the chemical-free, three-bath, wash-off process.

2. Experimental

2.1. Materials

The scoured and bleached, plain weave cotton fabric described previously [1] was used. Commercial samples of *Cibacron Yellow W-R* (C.I. Reactive Yellow 205), *Cibacron Red W-B* (C.I. Reactive Red 264) and *Cibacron Navy W-B* (C.I. Reactive Black 5, **5**) were kindly supplied by Ciba–Geigy and were used without purification. The structures of neither the aminochlorotriazine/vinyl sulfone C.I. Reactive Yellow 205 nor the bis(aminochlorotriazine/vinyl sulfone) C.I. Reactive Red 264 dyes have been disclosed in the Colour Index [21]. The dyeing auxiliary *Cibapon R* (modified polyacrylic acid Na salt [22]) was also generously provided by Ciba–Geigy.

2.2. Dyeing

Using the equipment described previously [1], 2% omf dyeings were carried out using the method shown in Fig. 1 [23].

2.3. Wash-off

At the end of dyeing, the samples were squeezed to remove surplus dye liquor and subjected to the two wash-off processes described below, at the end of which, the washed-off dyeings were rinsed in water, squeezed and allowed to dry in the open air.

2.3.1. Standard wash-off

This recommended, five-stage process [23] uses the proprietary wash-off agent, *Cibapon R* (Fig. 2).

2.3.2. Three-bath wash-off

Each of the three stages in this wash-off process (Fig. 3) was undertaken without using the proprietary wash-off agent.

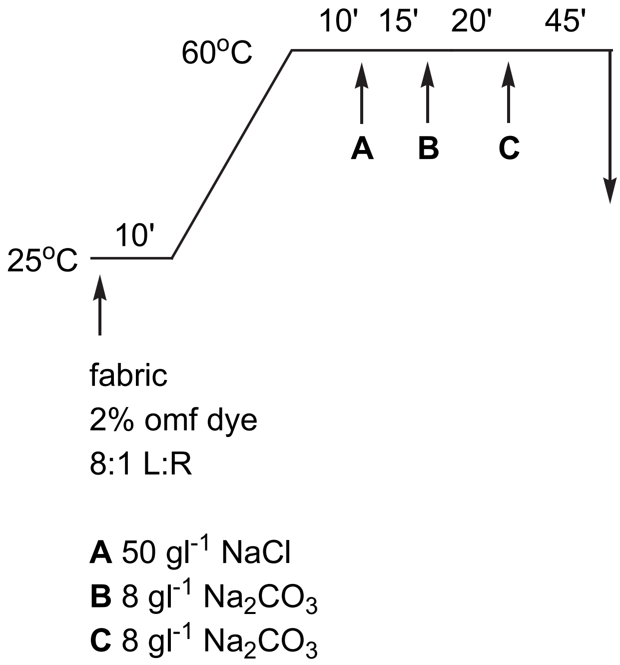

Fig. 1. Dyeing method for Cibacron W dyes.

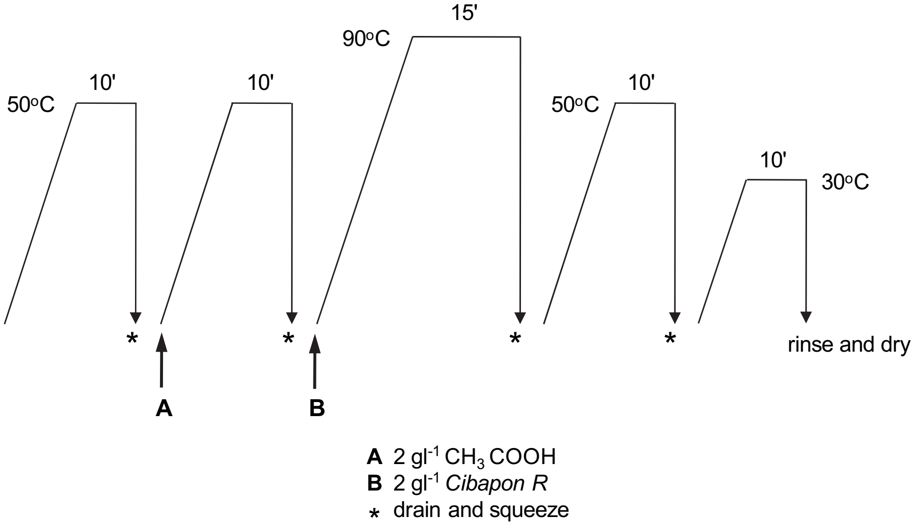

Fig. 2. Standard wash-off method.

2.4. Colour measurement

The equipment and procedures described previously [1] were used.

2.5. Wash fastness

The modified ISO 105:C06/C2 [24] method described previously [1] was used, according to which, dyeings were subjected to five, consecutive wash tests at 60 °C and 5 represents no colour change or staining.

2.6. Determination of BOD_5 and COD

The wastewater generated at the end of each rinse stage of the three wash-off methods used was analysed for BOD_5 and COD as described previously [1].

3. Results and discussion

As pointed out in the first part of this paper [1], as the constitution of very few contemporary reactive dyes is available, instead of relating results obtained to dye structure, this work was intended to generate indicative information on the behaviour of typical, modern reactive dyes. Hence, the three dyes employed in this part of the paper were selected arbitrarily, as typical examples of modern, homo- and heterobifunctional reactive dyes namely, bis (vinyl sulfone) (C.I. Reactive Black 5), aminochlorotriazine/vinyl sulfone (C.I. Reactive Yellow 205) and bis(aminochlorotriazine/vinyl sulfone) (C.I. Reactive Red 264).

3.1. Dyeings that received no wash-off

As mentioned, at the end of dyeing, cotton which has been dyed with reactive dyes is subjected to an aqueous wash-off treatment to remove surplus dye and dyeing auxiliaries so that the required colour, depth of shade, fastness, etc. can be obtained. Typically, wash-off treatments employ specific auxiliaries (eg surfactants, alkalis, etc.) and also consume large amounts of water. In order to determine the effectiveness of the three-bath, chemical-free wash-off method in improving the fastness of the three dyes on cotton, the fastness of the dyeings prior to wash-off was established. When 2% omf dyeings of each of the three dyes used were subjected to five, repeated wash tests at 60 °C, only moderately good fastness was observed, as evidenced by both the change in shade of the dyeings that occurred at the end of the five wash tests (Fig. 4) as well as the staining of the adjacent cotton component of the multifibre strip material by vagrant dye which had been removed from the dyeings during repeated washing (Fig. 5). Fig. 5 shows only the

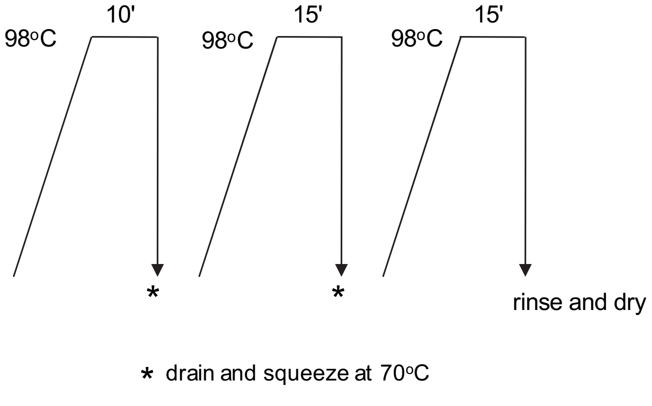

Fig. 3. Three-bath wash-off method.

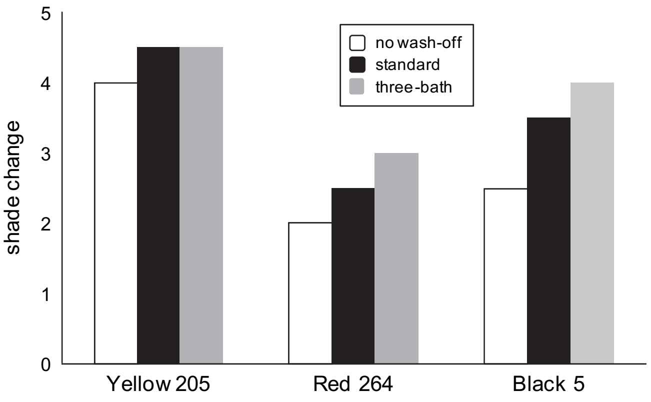

Fig. 4. Shade change obtained after five repeated wash tests.

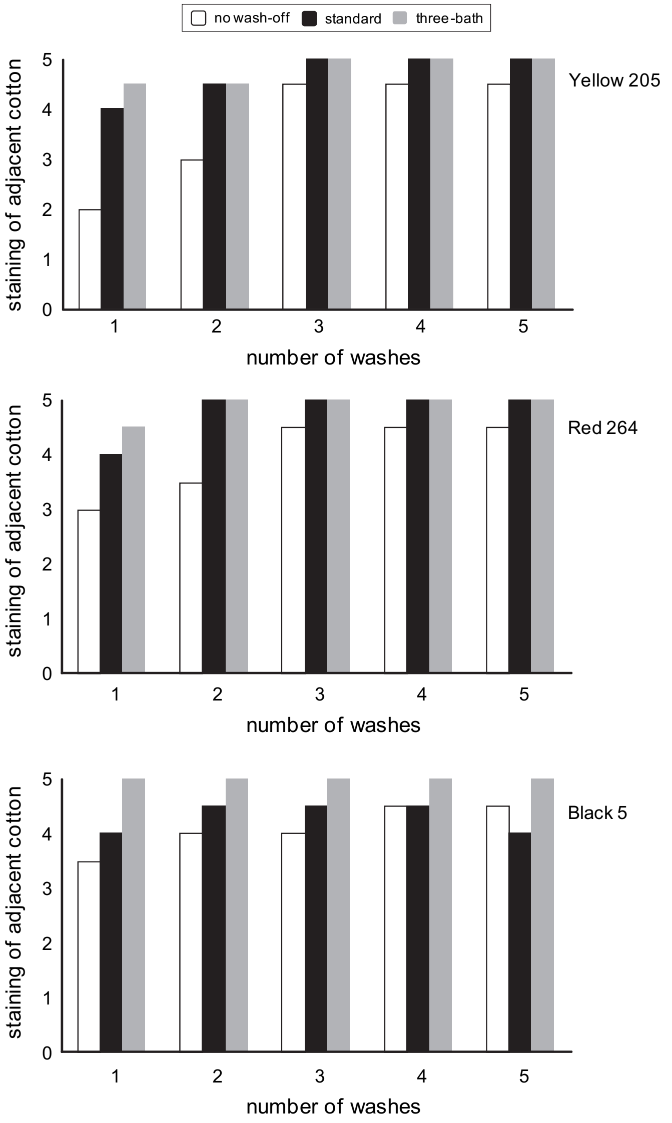

Fig. 5. Staining of adjacent cotton component after five repeated wash tests.

staining achieved for the cotton component as no staining was obtained for the adjacent wool, acrylic, polyester, nylon 6,6 and cellulose diacetate components. The high level of staining obtained for the adjacent cotton material was expected, as it is this type of fibre that the dyes are designed to be applied to and, therefore, towards which substrate the dyes display marked substantivity. The lack of staining recorded in the cases of the adjacent wool, acrylic, polyester, nylon 6,6 and cellulose diacetate components was anticipated in view of the inherent low substantivity of the reactive dyes towards such types of fibre.

Both the observed change in shade of the dyeings (Fig. 4) and staining of adjacent cotton material (Fig. 5) can be attributed to unfixed and/or hydrolysed dye having been removed from the dyed fabric during wash testing. This (unsurprising) result clearly demonstrates that, firstly, dye-fibre reaction was incomplete and that either/both unfixed (reactive) and hydrolysed forms of the dyes were present on the dyed substrates after dyeing and that these displayed marked substantively towards the cotton component of the adjacent multifibre strip material. It is also evident (Fig. 5) that the extent of staining of the adjacent cotton component achieved for the first two or so wash tests was noticeably worse than that obtained for the subsequent wash tests. These findings were expected because surplus dye present on the samples at the end of dyeing had not been removed by a wash-off process; hence, the observation that the extent of staining improved with increasing number of wash tests can be attributed to the first two or so washes having removed such surplus unfixed/hydrolysed dye.

The corresponding colour strength (K/S values), before and after wash testing, obtained for the dyeings which had received no wash-off (Fig. 6) provide a measure of the extent to which unfixed/hydrolysed dye was removed by repeated washing. The corresponding colorimetric data (Fig. 7) for the dyeings which had received no wash-off reveal that, as a result of repeated washing, both the yellow and red dyeings became redder in shade, although the chroma of the dyeings was reduced, whilst the black dyeing became slightly bluer in shade and underwent an increase in chroma; in addition, repeated wash testing increased the lightness of the dyeings, as might be expected from the observed loss of unfixed dye that accompanied washing. The finding that the λ_{max} of the dyeings (440, 520 and 600 nm for the yellow, red and black dyeings, respectively) were unchanged after five wash fastness tests demonstrate that repeated wash testing had had no marked effect upon the hue of the dyeings.

3.2. Washed-off dyeings

Dyeings which had been washed-off using the dye maker's recommended, five-stage method employing the modified polyacrylic acid, wash-off agent, *Cibapon R* (Fig. 2) displayed improved fastness to repeated wash testing at 60 °C, compared to those which had not been washed-off, insofar as, the extent of staining of the adjacent cotton fabric was reduced compared to dyeings which had not been washed-off (Fig. 5) and the extent of the change in shade which the dyeings underwent as a result of five washes was also reduced (Fig. 4). Improved fastness to repeated wash testing was also secured for the dyeings which had been washed-off using the three-bath, chemical-free process (Fig. 3), compared to dyeings which had not been washed-off, in terms of change in shade and staining of adjacent cotton (Figs. 4 and 5).

In terms of the staining of adjacent cotton, Fig. 5 shows that the three-bath wash-off process imparted higher fastness to the dyeing obtained using C.I. Reactive Black 5 for each of the five wash tests used and, in the cases of both the red and yellow dyes, was more effective for the first wash test. These results are reflected in the corresponding shade changes that accompanied repeated wash

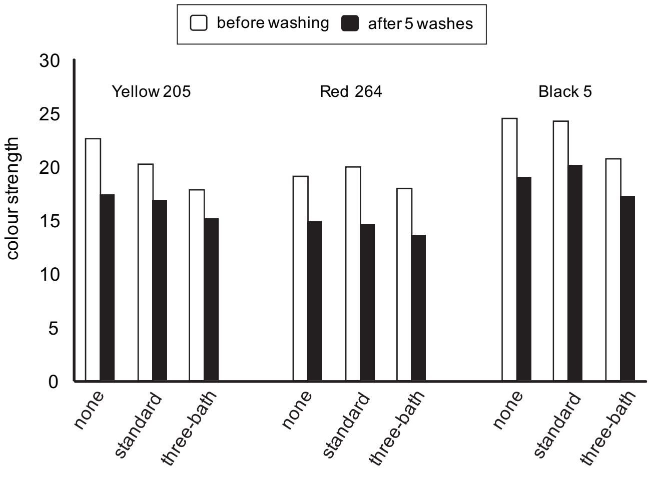

Fig. 6. Colour strength before and after five repeated wash tests.

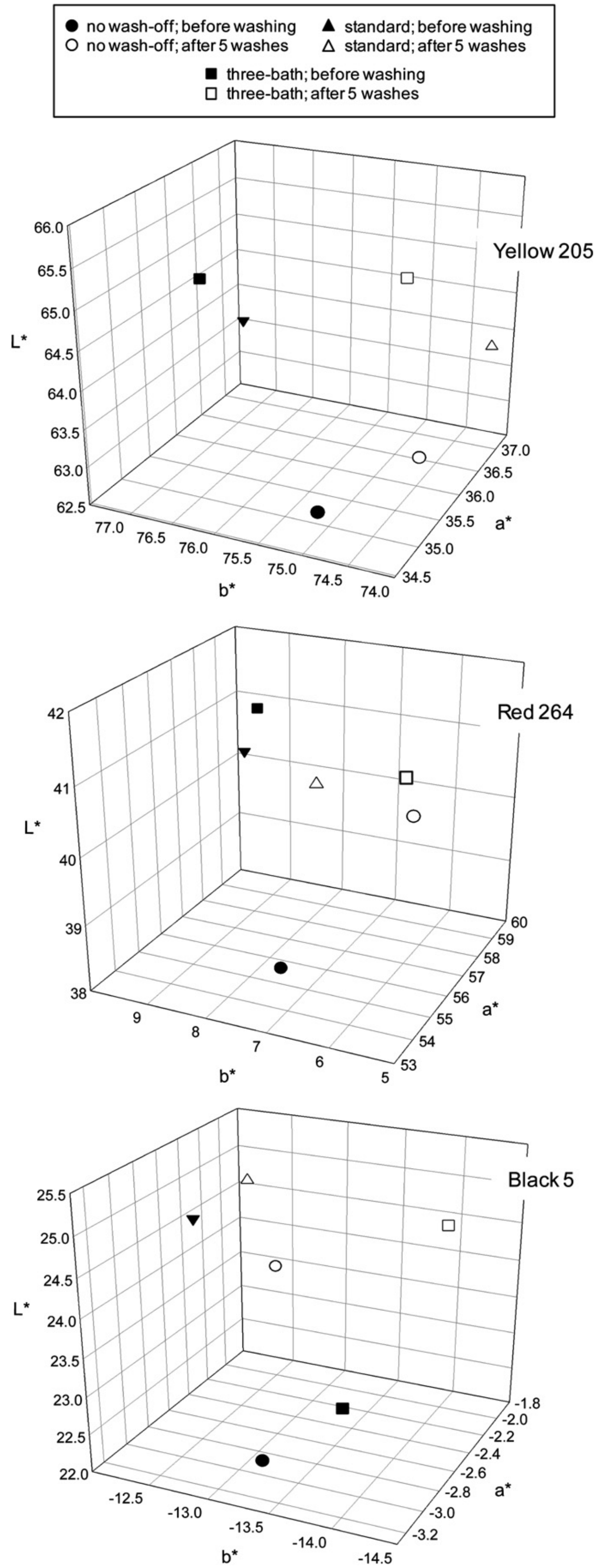

Fig. 7. Colorimetric parameters for dyeings before and after five repeated wash tests.

testing (Fig. 4), which show that the three-bath process was more effective than the standard wash-off method in the cases of the red and black dyes. These findings can be explained in terms of the effect of both wash-off processes on the depth of shade of the dyeings prior to fastness testing. The colorimetric data shown in Fig. 7 reveal that, in general, for the three dyes used, each of the wash-off methods reduced the depth of shade of the dyeings, compared to that of the unwashed-off dyeings, prior to repeated washing, as evidenced by the higher lightness (L*) values of the washed-off samples. This expected result is attributable to the wash-off processes having removed unfixed/hydrolysed dye. A further measure of the extent of this removal of unfixed dye prior to repeated wash testing is provided by the corresponding colour strength of the dyeings before and after wash testing (Fig. 6) from which it is apparent that each wash-off method reduced K/S before washing; it is also apparent that the three-bath wash-off process resulted in lowest colour strength. As wash fastness is inversely related to depth of shade, all other things being equal, it seems reasonable to suggest that the observed lower staining results obtained for both wash-off process are attributable to the lower K/S of the dyeings prior to wash testing.

When the colorimetric data obtained for the unwashed-off dyeings are compared to those secured for dyeings which had been subjected to the two wash-off methods (Fig. 7), it is evident that the effects of repeated washing on the hue and chroma of the dyeings were very similar, regardless of whether the samples had been washed-off or not. Repeated washing caused the yellow and the red dyeings to become redder in shade and also reduced the chroma of the dyeings, whereas the black dyeing became slightly bluer in shade and underwent an increase in chroma. In addition, the finding that the $\lambda_{\max}$ values for all of the dyeings were unchanged after five wash fastness tests (440, 520 and 600 nm for the yellow, red and black dyeings, respectively) demonstrate that repeated wash testing had no marked effect upon the hue of the dyeings.

3.3. *Environmental indicators*

3.3.1. *COD*

Three indicators were employed in this work to determine the environmental impact of the wash-off processes employed, namely, BOD$_5$, COD and COD/BOD$_5$ ratio [1]. The wastewater generated at the end of each wash-off bath was collected and analysed for BOD$_5$ and COD within 24 h of collection.

Fig. 8 shows the COD values obtained for each of the five stages of the standard wash-off process that used the proprietary wash-off agent, *Cibapon R*. As the COD value indicates the oxygen concentration that is required to oxidise all carbon compounds in a solution, then the COD values obtained can be attributed to, presumably, the presence of dye, the modified polyacrylic acid, wash-off agent, *Cibapon R*, the acetic acid used in the neutralisation stage as well as salts (eg CH$_3$COONa) thereof generated in the neutralisation step. Fig. 8 shows that the magnitude of the COD environmental indicator followed the general order:

second rinse >> third rinse <<< first rinse = fourth rinse > fifth rinse

The first rinse stage in a conventional wash-off of reactive dyeings lowers the often very high electrolyte concentration within the cotton substrate that arises from the dyeing process and also expedites the removal of the 'easily removed' unfixed/hydrolysed dye [1]. Fig. 8 shows that, for each of the three dyes used, sizeable dye removal occurred during the second rinse stage, which, for the particular dye types used, constitutes a neutralisation step using acetic acid. The finding that this particular wash-off stage generated wastewater which displayed by far the highest COD values can be attributed to not only removed dye but also the added CH$_3$COOH,

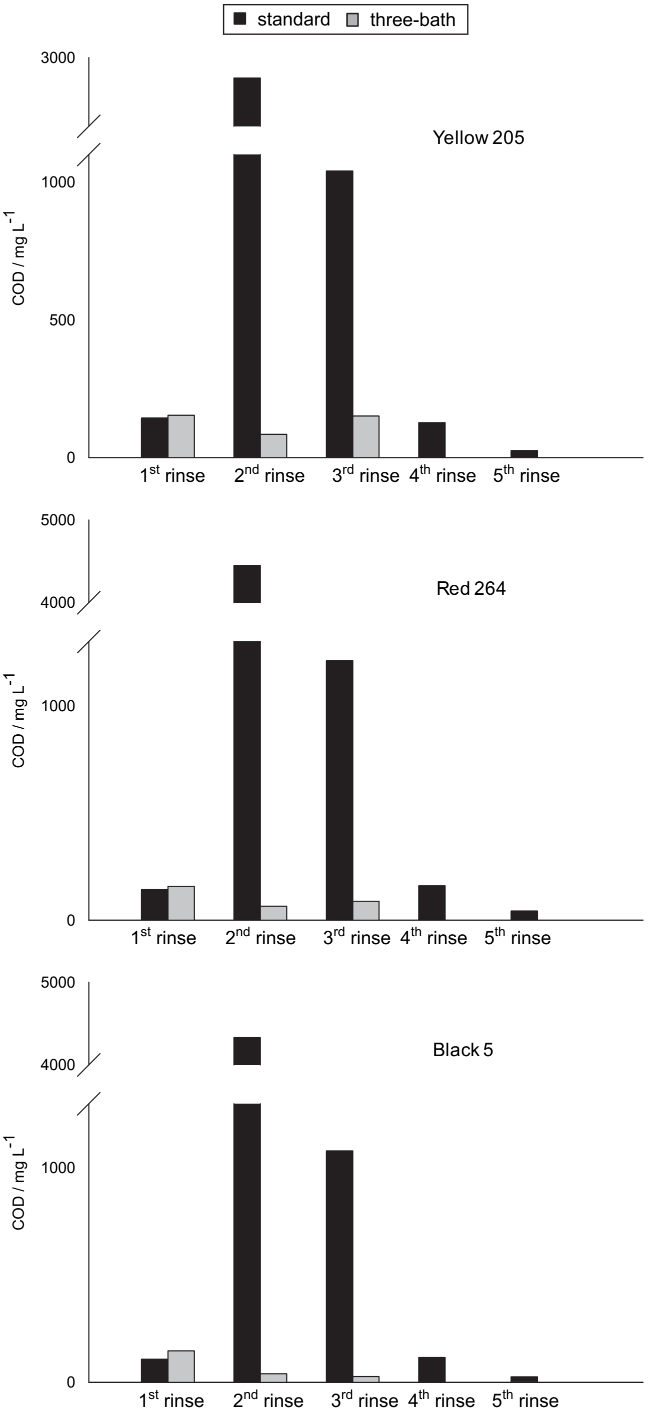

Fig. 8. COD of rinse baths.

as well as the various salts (eg CH$_3$COONa) produced during this neutralisation stage. As values of 500–1000 mg l^{-1} and <75 mg l^{-1} are typical for the COD values at the inlet and outlet, respectively, of a water treatment plant [25], the values of this parameter obtained for the second rinse stage for each of the three dyes used can be considered to be high, especially in the cases of the red and black dyes. The high COD values secured for the third rinse stage (Fig. 8) suggest that large amounts of unfixed dye were once again removed; however, as this particular stage of the standard wash-off also included treatment with the commercial wash-off agent *Cibapon R* at 90 °C, it is likely that the COD generated from the third rinse stage included a major contribution from the modified polyacrylic acid wash-off agent (Knudsen considers that some 70% of the COD load from a reactive dyeing wash-off process can be attributed to such auxiliaries [7]). In addition, residual salts, passed on from the previous rinse bath, may also have contributed to the high COD value secured for the third rinse stage. In a similar manner, the observation (Fig. 8) that the residual wastewater from the fourth rinse stage was of higher COD than that obtained from the final (fifth) rinse stage can be ascribed to the presence of both higher amounts of removed dye and/or the wash-off agent itself.

The three-bath wash-off process shown in Fig. 3, was devised in an attempt to reduce both the amount of water and chemicals consumed in reactive dye wash-off [1]. In this process, each rinse stage used water only at 98 °C and did not employ the proprietary wash-off agent *Cibapon R* that was used in the dye maker's recommended, standard, five-stage wash-off method (Fig. 2). When the 2% omf dyeings were washed-off using this particular process the COD values obtained (Fig. 8) for the three stages of the process generally followed the order:

first rinse > second rinse > third rinse

This observed reduction in COD values from the first to the final (third) rinse stage can be attributed to a corresponding reduction in the amount of dye removed. Fig. 8 also shows that for each of the three dyes used, the COD values obtained for the first rinse stage of the three-stage wash-off process were slightly higher than those obtained for the corresponding standard wash-off process. This finding suggests that the first rinse in water at 98 °C used in the three-stage wash-off process, was more effective in removing unfixed/hydrolysed dye than was the 70 °C first rinse in water employed in the standard wash-off method. This result is attributable to the higher dye solubility and greater extent of fibre swelling at the higher temperature. It is also evident that comparatively much lower values of COD were obtained for each of the three stages of the chemical-free, wash-off method (Fig. 8) than the corresponding first three rinse stages of the standard wash-off, presumably due to the lack of both CH$_3$COOH and modified polyacrylic acid wash-off agent. In the context of the previously mentioned values of COD being typically <75 mg l^{-1} at the outlet of a water treatment plant, the values of this parameter obtained for each of the three rinse stages of the three-bath wash-off method were not especially high and, at each stage, were well below the lower limit of 500 mg l^{-1} likely to be found at the treatment inlet, for all three dyes used.

3.3.2. BOD$_5$

BOD$_5$, which quantifies how rapidly biological organisms consume oxygen in a body of water, is indicative of the quality of a water source, even though it does not constitute an accurate quantitative test. The BOD$_5$ values obtained for each of the wash-off stages using the standard and three-bath wash-off methods are shown in Fig. 9. It is evident that the values of this particular environmental indicator secured for the red and black dyeings were substantially greater than those obtained for the yellow dye. As BOD$_5$ values are, typically, 400–1000 mg l^{-1} at the inlet and <50 mg l^{-1} at the effluence of the plant [25], the values obtained for the residual second and third rinse stages in the cases of the red and black dyes (Fig. 9) are especially high, in contrast to those secured for the corresponding rinse stages of the yellow dye. It is also apparent that for the red and black dyes, the magnitude of the BOD$_5$ values followed the general order:

second rinse > third rinse <<< first rinse = fourth rinse > fifth rinseand in doing so, were very similar to that obtained for the COD values (Fig. 8). Hence, the finding that the second stage generated wastewater which displayed by far the highest BOD$_5$ values can be attributed to not only removed dye but also to added CH$_3$COOH, as well as the various salts (eg CH$_3$COONa) produced during this

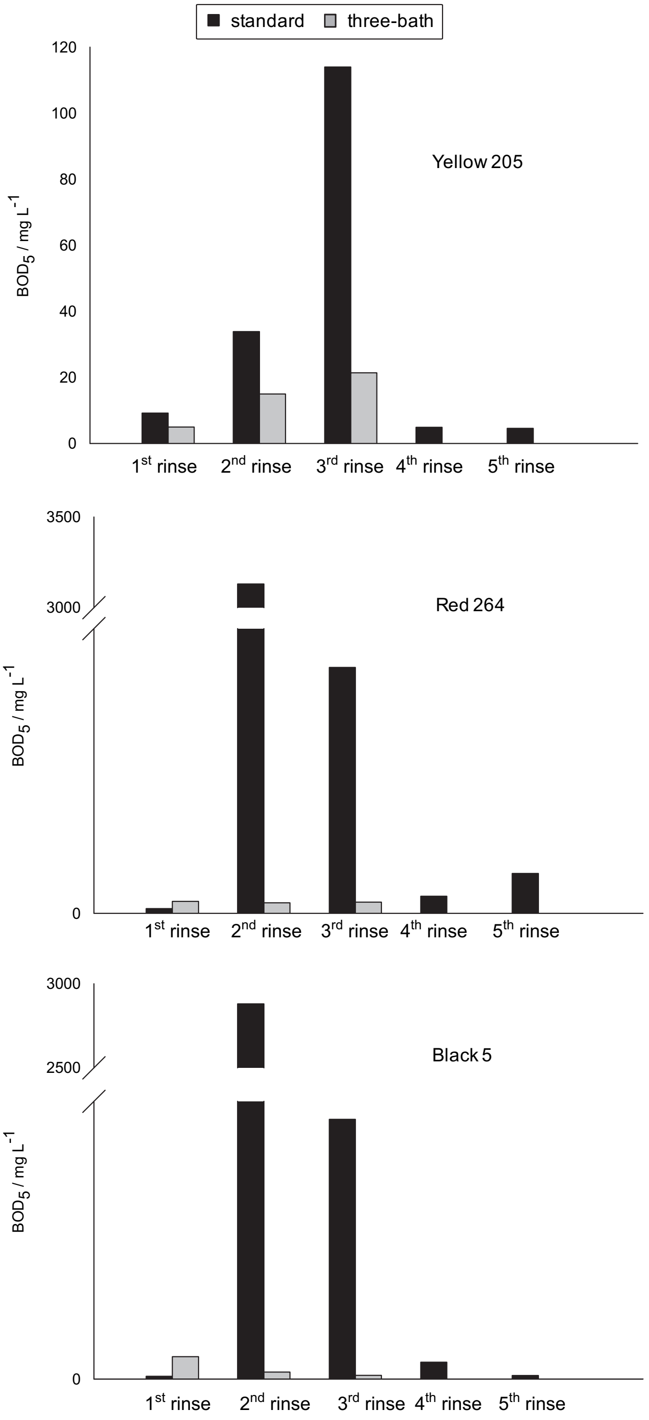

Fig. 9. BOD_5 of rinse baths.

neutralisation stage. The observation that the second highest BOD_5 values were obtained for the third rinse stage, which employed *Cibapon R*, reflects not only the efficacy of this particular, high temperature (90 °C) treatment in removing unfixed dye but also the presence of the modified polyacrylic acid wash-off agent in the residual wastewater. In a similar manner, the combined use of 90 °C and wash-off agent may well explain why the highest BOD_5 value achieved for the yellow dye was secured for the third (90 °C) rinse stage.

As BOD_5 values are an indication that wastewater contains organic material that can be oxidised but which is not biodegradable [1], the observed marked difference between the magnitude of the BOD_5 values obtained for the yellow dye and the values obtained for the red and black dyes (Fig. 9) indicates that the quality of the wastewater obtained from the yellow dyeings was lower than that from either the red or the black dyeings. A comparison of Figs. 8 and 9 shows that the values of COD obtained for the yellow dye were much higher than the corresponding BOD_5 values, for each of the five wash-off stages used, which is indicative of wastewater that contains oxidisable organic material that is not biodegradable. As BOD_5 is determined biologically, it accounts only for compounds in

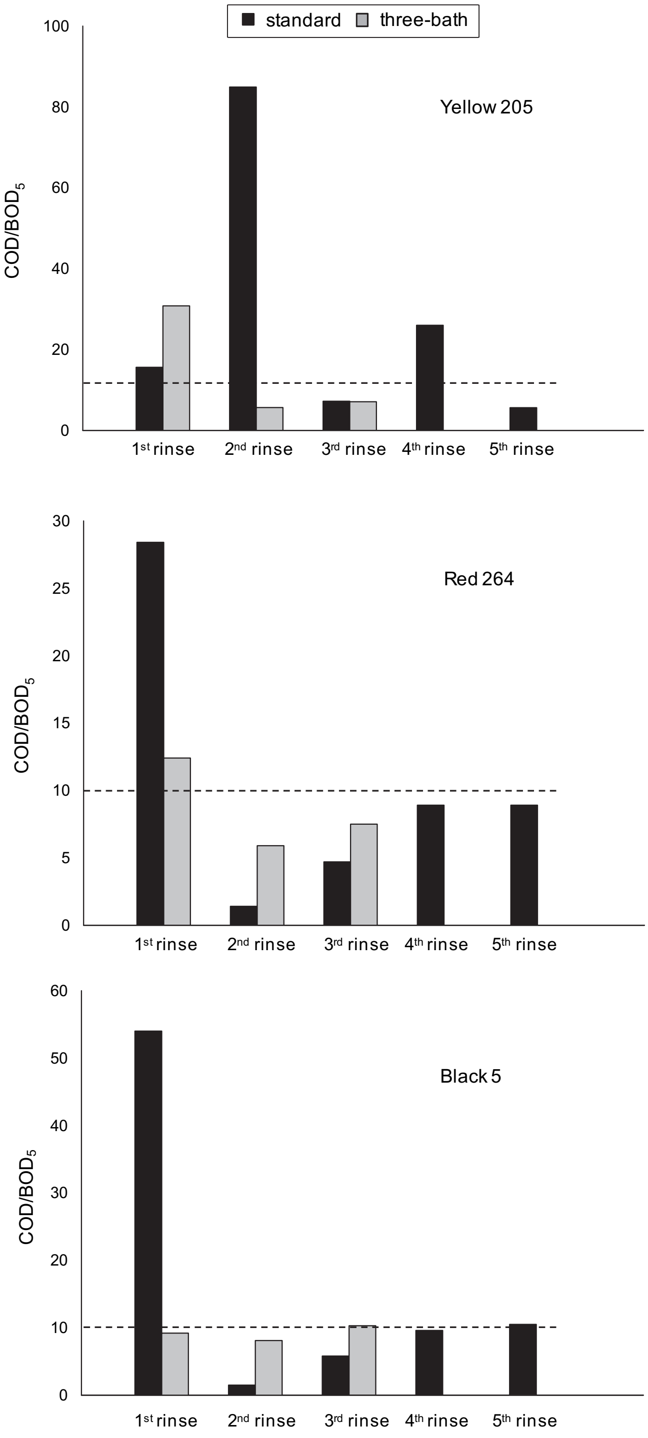

Fig. 10. COD/BOD_5 of rinse baths.

Table 1
Environmental indicators for combined rinse stages.

Wash-off	C.I. Reactive Yellow 205		C.I. Reactive Red 264		C.I. Reactive Black 5	
	BOD_5/mg l^{-1}	COD/mg l^{-1}	BOD_5/mg l^{-1}	COD/mg l^{-1}	BOD_5/mg l^{-1}	COD/mg l^{-1}
Standard	166.5	4217.1	3416.6	6004.2	3083.6	5659.8
Three-bath	41.5	389.8	35.5	309.7	23.7	214.4

wastewater that are biodegradable whereas COD measures the oxygen demand of organic compounds in wastewater. Hence, a sample of wastewater that contains material which can be oxidised but which is not biodegradable, will have a high COD but a low BOD_5. This was clearly the case for the yellow dye, both for the standard and three-bath wash-off methods.

The results in Fig. 9 also show that the BOD_5 values obtained for the three-bath wash-off process were considerably lower than those obtained for the standard wash-off method, for each dye used. As in the above discussion of the values of COD obtained (Fig. 8), this can be attributed to the absence of both CH_3COOH and modified polyacrylic acid wash-off agent in the case of the three-bath process. In the context of the previously mentioned values of BOD_5 being typically <50 mg l^{-1} at the outlet of a water treatment plant, the values of this parameter obtained for each of the three rinse stages of the chemical-free wash-off method were quite low and substantially lower than the lower limit of 400 mg l^{-1} likely to be found at the treatment inlet, for each of the dyes used.

3.3.3. COD/BOD_5

As previously discussed [1], the COD/BOD_5 ratio can be considered as an indicator of the relative biodegradability of wastewater, an inverse relationship existing between the ratio and biodegradability. Although no agreed COD/BOD_5 index applies to different types of wastewater, a COD/BOD_5 ratio of 3–7 implies moderate biodegradability of wastewater, whilst values ≥ 10 are indicative of biologically untreatable wastewater [26] and recourse to an additional treatment of the organic components may be required so as to achieve a 'biodegradable' COD/BOD_5 range of <3 [26].

In the case of the standard wash-off process, Fig. 10 shows that the wastewater generated from the first rinse stage, in the cases of the red and black dyes, displayed high COD/BOD_5 ratios, which can be attributed to the presence of removed dye. In the case of the yellow dye, the second rinse stage gave rise to the highest COD/BOD_5 ratio; as this rinse stage also comprised neutralisation with CH_3COOH, the high ratio obtained may be to not only removed dye but also the added CH_3COOH, as well as the various salts (eg CH_3COONa) produced during this neutralisation stage. In the context of the biodegradability of the liquor obtained for the residual rinse stages, the dotted lines in Fig. 10 show a COD/BOD_5 ratio of 10, as this value relates to wastewater which cannot be biologically treated [26]. For the red and black dyes, the majority of the five rinse stages comprised liquor of moderate biodegradability (ie ratio <10) whereas for the yellow dye, three of the rinse stages comprised liquor of low biodegradability (ie ratio >10), with the result that a treatment to lower the amount of chemically treatable organic components might well be required in order to achieve a 'biodegradable' COD/BOD_5 ratio range of <3 [26].

For the three-bath wash-off process (Fig. 10) the COD/BOD_5 ratios were, for all three dyes used, much lower than those obtained for the corresponding stages of the standard wash-off process. This finding is interesting, as the lower colour strength (Fig. 6) and higher L^* values (Fig. 7) of the dyeings which had been washed-off using this particular process show that more dye had been removed by the high temperature, three-bath method. Hence, the COD/BOD_5 values in Fig. 10 were not simply related to the amount of dye present in the rinse bath, because if this were the case then the ratios for the three-bath wash-off should have been greater than those of the standard method. The lower COD/BOD_5 ratios obtained for the chemical-free wash-off process may therefore be attributable to the absence of the commercial wash-off agent and CH_3COOH. The biodegradability of the liquors from the three rinse stages (Fig. 10) ranged from low in the case of the first rinse to moderate for the last two rinse stages.

As it is common in industry for wastewaters obtained from different processes to be combined, the COD and BOD_5 values that were obtained for each rinse stage were combined so as to obtain the total environmental load generated by each wash-off method (Table 1). It is evident that the combined COD and BOD_5 loads for the three-bath wash-off process were considerably lower than those for the standard wash-off method. The combined COD secured for the five standard wash-off stages were particularly high for each of the three dyes, bearing in mind typical COD of 500–1000 mg l^{-1} at the inlet and <75 mg l^{-1} at the outlet of a treatment plant [31] whereas, in contrast, the combined COD obtained for the three-bath process were well below those which might typically be obtained at the outlet of a water treatment plant. The combined BOD_5 secured for the three-bath process were, for each dye used, lower than that recorded for the recommended, standard wash-off process.

4. Conclusions

The replacement of the commercial wash-off agent used in the five-stage, standard wash-off process with three, high temperature, water-only rinses had no detrimental effect on the colour and repeated wash fastness of the dyeings, although the colour strength of the washed dyeings which had been subjected to the three-bath wash-off was slightly lower than that achieved using the standard wash-off process. These findings agree with those obtained in the first part of the paper [1] that used three bis(aminochlorotriazine) dyes on cotton. The use of three, boiling water rinse stages reduced considerably, both the combined COD and, especially, BOD_5 compared with the standard method, with no increase in COD/BOD_5 ratio. These findings also concur with those secured using the three homobifunctional dyes employed in the first part of the paper [1], although the COD and BOD_5 values obtained for these particular dyes were much lower than those recorded for the bis(vinyl sulfone), aminochlorotriazine/vinyl sulfone and bis(aminochlorotriazine/vinyl sulfone) dyes used in this part of the paper. Hence, as was proposed for bis(aminochlorotriazine) dyes [1], not only does the three-bath wash-off method offer potential savings in water usage, compared to the standard method, but also eliminates the need for chemicals to be used in wash-off.

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